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Atomic-layer surface reaction of chlorine on Si and Ge assisted by an ultraclean ECR plasma

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Abstract

Atomic-layer surface adsorption and reaction of chlorine on Si(100) and Ge(100) as well as $\text{Si}_{0.5}\text{Ge}_{0.5}$ (100) assisted by low-energy Ar^+ ion irradiation were investigated using an ultraclean ECR plasma system with surface analysis by XPS and FTIR/RAS. Hydrogen termination on Si and Ge prepared by HF-treatment or annealing in H_2 was removed by Ar^+ ion irradiation, and that on Ge was removed, while not on Si, only by the chlorine molecular supply. By repeating alternate chlorine molecular supply ($\geq 0.02 \text{ Pa} \cdot \text{s}$) and Ar^+ ion irradiation ($\sim 4 \times 10^{15} \text{ cm}^{-2}$), atomic-layer etching of Si, Ge, and $\text{Si}_{0.5}\text{Ge}_{0.5}$ was observed with a saturated etch rate per cycle of 1/4 atomic-layer thickness. When Ar^+ ion irradiation was increased further under a condition of saturated chlorine molecular adsorption, the etch rate per cycle tended to increase with Ar^+ ion irradiation up to a saturation value of the single atomic-layer thickness. The Ge atoms indicated a higher reactivity than the Si atoms in the atomic-layer etching. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Atom–solid reactions; Electron bombardment; Germanium; Halogens; Ion etching; Plasma processing; Silicon

1. Introduction

Accurate knowledge on the characteristics of the atomic-layer surface adsorption and reaction of chlorine on a Si–Ge system is important for controlling etching process of future Si–Ge devices, e.g. single or multiple quantum well or superlattice structure devices made of the group IV elements [1]. Moreover, the reaction should be induced by the directional incidence of ions because directional etching is essential for device fabrication with well-defined dimensions (see, for example, Ref. [2]). Using a conventional dry etching process, since adsorption and reaction occur simulta-

neously, it is difficult to obtain an atomic-layer precision. However, by controlling the adsorption and reaction, an atomically precise etching process can be expected.

By repeating alternate chlorine supply and Ar^+ ion irradiation in several hundred cycles, the self-limited fractional atomic-layer etching per cycle was observed for Si and Ge using an ultraclean ECR plasma system [3,4]. In the present work, the atomic-layer surface adsorption and reaction of chlorine on Si, Ge as well as $\text{Si}_{0.5}\text{Ge}_{0.5}$ assisted by low-energy Ar^+ ion irradiation has been investigated using an ultraclean ECR plasma system. The removal of hydrogen termination of the initial surface as well as the atomic-layer etching characteristics are compared for Si, Ge and $\text{Si}_{0.5}\text{Ge}_{0.5}$.

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2. Experimental

For atomic-layer reaction, an ultraclean ECR plasma system was used, the details of which were described previously [5,6], but in short, the most important feature is that the system is ultraclean and it supplies low energy ions. The plasma can be synchronously turned off for supplying only chlorine molecules on to the surface and continuously turned on for supplying radicals, in order to investigate adsorption characteristics difference of molecules and radicals. For atomic-layer etching with only chlorine molecules being supplied, Ar^+ ions generated cyclically by a 2.45 GHz microwave in the ECR plasma generating chamber are transported by the divergent magnetic field and irradiated on to the wafer in the reaction chamber by opening and closing the shutter in front of the wafer. Ultraclean chlorine gas is supplied into the reaction chamber anti-synchronously with the plasma generation, so that only chlorine molecules without radicals are supplied on the surface. Pressures during the process were monitored by a Baratron gauge. The total pressure (P_{total}), which is nearly equal to the Ar partial pressure, is ~ 0.8 Pa.

The substrates used were Si(100), ~ 1600 and ~ 5000 Å thick epitaxial Ge and $\text{Si}_{0.5}\text{Ge}_{0.5}$ films deposited on Si(100) at 350°C and 550°C , respectively, by low pressure CVD [7–9]. The Si substrate was cleaned by several cycles in a $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ solution, and the Ge and $\text{Si}_{0.5}\text{Ge}_{0.5}$ substrates were in trichloroethylene and in ethanol, and then all were rinsed with DI water. Then, the substrate was dipped in diluted HF, rinsed again with DI water and dried with a N_2 blow just before loading into the ECR system. After the process, the surface was analyzed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red reflection adsorption spectroscopy (FTIR/RAS). An SiO_2 film patterned by a conventional lithography technique was used as a mask for measuring the atomic-layer etching depth after several hundred cycles of etching.

3. Results and discussion

On the initial Si(100) surface after diluted HF treatment, it is known [10,11] that hydrogen ter-

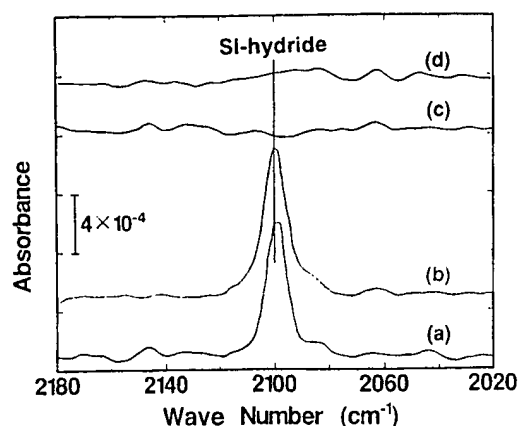


Fig. 1. FTIR/RAS spectra of the Si(100) surfaces (a) annealed in H_2 , and subsequent exposure to (b) Cl_2 molecules, (c) chlorine radicals, or (d) Ar^+ ion irradiation.

mination is formed, which is usually composed of Si-monohydride, -dyhydride and -trihydride. These hydrogens were removed not by a chlorine molecular supply but by a chlorine radical supply, and ECR Ar^+ ion irradiation also resulted in the removal of the hydrogen termination. Similar hydrogen removal characteristics were observed on the Si-monohydride dimer structure [12,13] prepared by annealing in H_2 at 700°C as shown in Fig. 1. These results indicate that hydrogen termination both on Si(100) and dimerized Si(100) shows almost the same reactivity with chlorine supply and Ar^+ ion irradiation.

The results for the similar reactivity investigation for Ge(100) are shown in Fig. 2. Since the FTIR Ge-hydride peak after diluted HF treatment was low, the Ge substrate was annealed in H_2 at 350°C for the investigation, where the apparent FTIR Ge-H peak is observed even after a few minutes of air exposure [14] as shown in Fig. 2a. The molecular chlorine supply is sufficient to remove hydrogen from the Ge surface (Fig. 2b), as well as Ar^+ ion irradiation (Fig. 2c). This indicates that hydrogen on the Ge surface is more reactive with chlorine than that on the Si surface. A higher reactivity of Ge-hydride has also been demonstrated by its stability against air exposure [14]. Considering these results from the point of view of the atomic-layer etching, it is expected that the

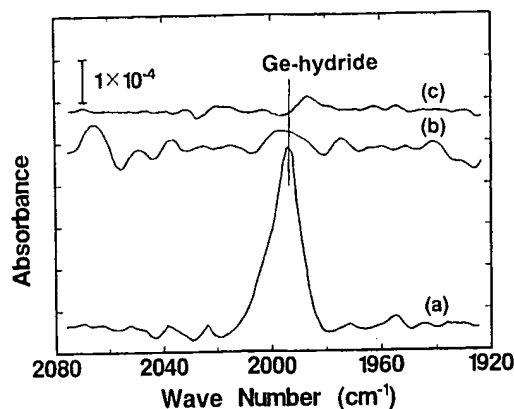


Fig. 2. FTIR/RAS spectra of the Ge(100) surfaces (a) annealed in H_2 , and subsequent exposure to (b) Cl_2 molecules, or (c) Ar^+ ion irradiation.

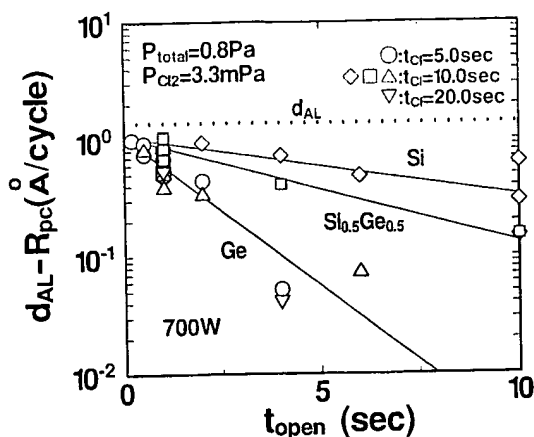


Fig. 3. Ar^+ ion irradiation time (t_{open}) dependence of $d_{AL} - R_{pc}$ for Ge (\circ , Δ , ∇), $Si_{0.5}Ge_{0.5}$ (\square) and Si (\diamond). The chlorine supply time is 5 s (\circ), 10 s (Δ , \square , \diamond) and 20 s (∇).

etching can be initiated by Ar^+ ion irradiation without any influence of the initial hydrogen termination.

Fig. 3 shows the dependence of the atomic-layer thickness (d_{AL}) minus the etch rate per cycle (R_{pc}) on the Ar^+ ion irradiation time (t_{open}) for Ge, $Si_{0.5}Ge_{0.5}$ and Si, where the difference of d_{AL} for Ge, $Si_{0.5}Ge_{0.5}$ and Si is only about 5%. It is seen that at the short t_{open} , R_{pc} is a quarter of d_{AL} for each substrate, which is controlled by saturation adsorption of chlorine molecules and a rapid ion-

induced reaction. This fractional nature of R_{pc} was explained for Si by considering the bond structure of the Si(100) surface [15]. Since each of the plots in Fig. 3 aligns along a straight line, R_{pc} increases with t_{open} , tends to saturate to d_{AL} , and is expressed by the following equation, assuming another slow type of simple Ar^+ ion-induced reaction:

$$R_{pc} = d_{AL} \{1 - (3/4) \exp[-(k_i \cdot J_{ieff}/n'_0) \cdot t_{open}]\} \times [n'_0 = (3/4)n_0] \quad (1)$$

where k_i is the reaction efficiency constant, J_{ieff} is the effective incident Ar^+ ion flux density, and n_0 is the initial surface atom density. Although the reproducibility of the data for Si and $Si_{0.5}Ge_{0.5}$ was less than that for Ge due to a more severe oxidation influence, the Ar^+ ion-induced reaction efficiency for Si and $Si_{0.5}Ge_{0.5}$ seems to be lower than that for Ge. For Ge, by comparing the atomic-layer etching rate and the energy distribution of Ar^+ ions at the microwave power of 700 W and 350 W, it was roughly estimated that one Ge atom is etched by an irradiation of ~ 10 Ar^+ ions with an energy higher than the order of ~ 13 eV [4].

At a short shutter opening time of 0.2–0.5 s, the atomic-layer etching rate per cycle for Ge scarcely depended on the chlorine supplying time, which indicates that the chlorine adsorption on Ge is saturated within the present experimental conditions. In the case of Si, the chlorine supply time dependence was observed, which is very well expressed by a simple Langmuir-type adsorption equation [16]. This result suggests that chlorine adsorption on to the Ge surface is faster than that on to the Si surface, i.e. Ge has a higher activity of chlorine adsorption than Si.

The Ge 3d XPS spectra of the $Si_{0.5}Ge_{0.5}$ surface before and after atomic-layer etching are compared in Fig. 4. It can be seen that the peak intensity after atomic-layer etching is lower than that before atomic-layer etching, indicating a selective removal of Ge atoms at the outermost surface. This suggests a higher desorption reactivity of the Ge atoms than that of the Si atoms, whereas the surface flatness was not so severely influenced.

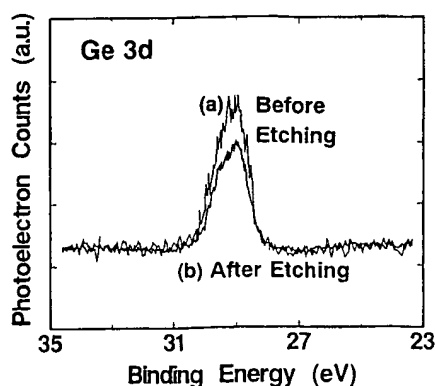


Fig. 4. Ge 3d XPS spectra of the $\text{Si}_{0.5}\text{Ge}_{0.5}$ surface (a) before and (b) after 30 cycle atomic-layer etching with chlorine supply quantity ($t_{\text{Cl}} \cdot P_{\text{Cl}_2}$) of $0.033 \text{ s} \cdot \text{Pa}$ and Ar^+ ion irradiation time (t_{open}) of 10 s. Each spectrum is normalized with the Si 2p spectrum intensity.

4. Conclusions

Atomic-layer surface adsorption and reaction of chlorine on Si(100) and Ge(100) as well as $\text{Si}_{0.5}\text{Ge}_{0.5}$ (100) assisted by low-energy Ar^+ ion irradiation were investigated using an ultraclean ECR plasma system with surface analysis by XPS and FTIR/RAS. Hydrogen termination on Si and Ge was removed by Ar^+ ion irradiation, and that on Ge was removed, while not on Si, only by the chlorine molecular supply. By repeating alternate chlorine molecular supply and Ar^+ ion irradiation, atomic-layer etching of Si, Ge, and $\text{Si}_{0.5}\text{Ge}_{0.5}$ was observed with a saturated etch rate per cycle of 1/4 atomic-layer thickness at a short irradiation time. When Ar^+ ion irradiation was increased further under conditions of saturated chlorine molecular adsorption, the etch rate per cycle tended to increase with Ar^+ ion irradiation up to a saturation value of the single atomic-layer thickness. The Ge atoms indicated a higher reactivity than the Si atoms in the atomic-layer etching.

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